Asian Journal of Chemistry; Vol. 36, No. 10 (2024), 2231-2245

ASIAN JOURNAL OF CHEMISTRY

https://doi.org/10.14233/ajchem.2024.32291

REVIEW

Magnetostructural Studies of Dinuclear Ni(II) Complexes with Tridentate NNO Chelator Schiff Base Ligands Originating from N-Substituted Diammines and Salicyldehyde or its Analogues: A Review

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Received: 11 July 2024; *Accepted*: 7 September 2024; *Published online*: 30 September 2024; AJC-21752

Considering its significant single-ion zero-field splitting and distinctive spin magnetic moment, nickel(II) complex is frequently utilized as a paramagnetic center in the synthesis of magnetic complexes. In this review, the magnetostructural features of dinuclear nickel(II) complexes of tridentate Schiff base ligands with NNO chelator resulting from several N-substituted diamines and salicyldehyde or its analogus aldehydes is discussed. A perfect combination of a tridentate Schiff base together with bridging coligands produces a large number of complexes with fascinating magnetic properties. The structural diversity of the Ni(II) complexes with NNO blocking Schiff bases are mostly directed by both the coordination number of the metal ions and different bridging modes of the co-ligands like azide, nitrate, thiocyanate, carboxylates, *etc*. The relationship between magnetic exchange interaction (*i.e.* ferromagnetic or antiferromagnetic) with bonding parameters such as Ni···Ni separation, Ni–O–Ni angles have also been analyzed. This review is focused on the structural aspects as well as the magnetic characterization of nickel(II) dimmers of tridentate Schiff bases having NNO donor sets to establish a magnetostructural correlation.

Keywords: Nickel(II) complexes, Schiff bases, Tridentate NNO donor, Magnetic characterization, Magnetostructural correlation.

INTRODUCTION

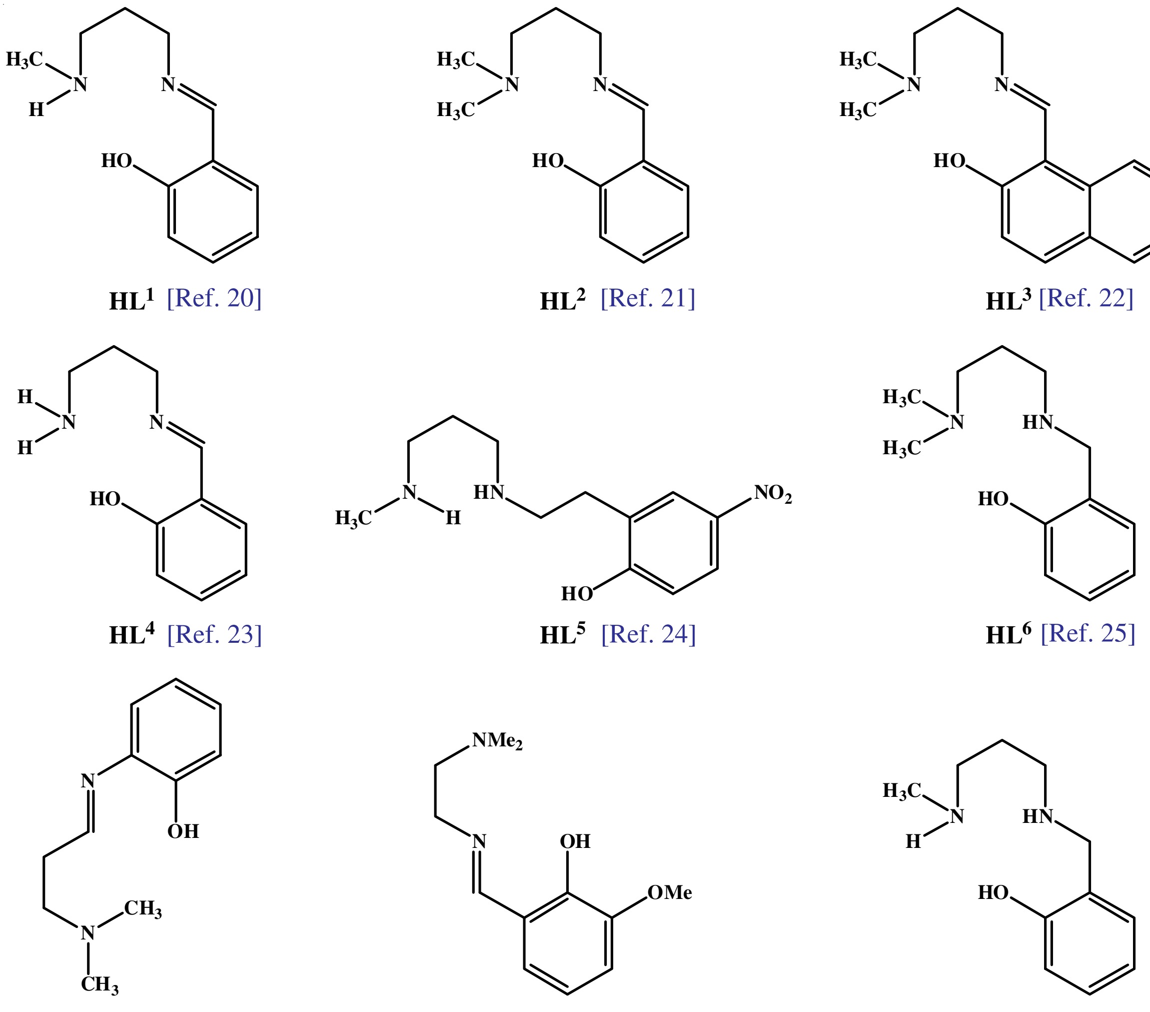
An intriguing field of study in chemistry is the structural and magnetic characteristics of dinuclear nickel(II) complexes of tridentate NNO donor Schiff base ligands with a range of bridging polyatomic anions (*e.g.* azide, nitrate, thiocyanate, carboxylates, *etc.*) [1,2]. The rising possibility of dinuclear phenoxido bridged nickel(II) complexes with NNO donor sites to serve as structural, electrical and catalytic replica of metalloenzyme urease has led to substantial research into this field [3-5]. Polynuclear nickel(II) complexes have been synthesized using the tridentate NNO donor Schiff bases generated from salicylaldehyde, which have the ability to bridge two metal ions through the phenoxido oxygen in presence of different bridging anionic coligands [6-10]. The coexistence of a polyatomic bridging moiety along with a NNO donor Schiff base in a complex makes the prediction of its structure exceedingly challenging. There are too many variables to take into account in these situations. Therefore, these kinds of NNO donor Schiff base ligands in combination with different polyatomic anions are a great way to create a variety of structural topologies and they are also very helpful in terms of magnetic coupling [7].

The magnetostructural correlation of these species have been identified, revealing the fascinating patterns. The nickel (II) complexes in consideration are dimeric and have octahedral coordination. These complexes also contain thiocyanate ligands in an end-on orientation [11,12] as well as end-on azide [13] and cyanate bridges, ferromagnetic interactions have been observed to predominate. The bridging Ni-O-Ni angle is shown to be the primary factor regulating the exchange coupling in phenoxido bridged dinuclear nickel(II) complexes [14]. Based on the outcomes of experiments, it is suggested that for phenoxido bridged nickel(II) complexes, ferromagnetic coupling takes place if the average Ni-O-Ni angles are between approximately 93.5º and 99.0º [15]. At larger angles, however, the magnetic orbitals' spin delocalization will be amplified, leading to the antiferromagnetic interactions [16]. In order to synthesize ferromagnetic Ni(II) complexes, it is important to reduce the bridging angle below these crucial values. The majority of dinickel(II) complexes reported in the literature that involve a Ni_2O_2-bridging moiety are linked antiferromagnetically [7,17,18]. It is very interesting to observe that together with two μ_2-phenoxido bridges, if an additional bridge is present over there, this additional bridge is crucial in reducing the Ni-O-Ni bridging angles under the critical one and changing the coupling from antiferro to ferromagnetic one [19].

A more thorough examination of the structural elements influencing the bridging angles reveals that bigger bridging angles are typically formed by monodentate [12,14] or chelated coligands (*e.g.* nitrite, nitrate, *etc.*) [9,10] in di-μ_2-phenoxido bridged nickel(II) complexes. In certain compounds, the phenoxido bridges are accompanied by an extra bridge in the form of a *syn-syn* carboxylato [15,16] or bidentate nitrito ligand [17]. Despite this, the compounds remain antiferromagnetically linked because the angle is greater than the critical value. In contrast, the di-μ_2-phenoxido bridged compounds become ferromagnetically coupled when a single atom (*e.g.* water or μ_{11}-azido) serves as an extra bridge between the two Ni(II) centres, causing the bridging angles to drop below the critical value [9,11,13,18].

This review provides a brief overview of the synthesis, structural elucidation, magnetic characterization of dinuclear nickel(II) complexes with NNO donor Schiff base ligands. Furthermore, this study clarifies the function of several bridging co-ligands (*e.g.*, NO_3^-, NO_2^-, N_3^-, $PhCO_2^-$, *etc.*) in establishing the magnetic contacts of such Ni(II) complexes. An attempt is made to shed some light on the magnetostructural correlation of dinuclear Ni(II) complexes with tridentate NNO donor Schiff base ligands. Hence in short, only those nickel (II) Schiff base complexes were considered which show the interesting magnetic properties.

Choice of ligands: Only the tridentate Schiff base ligands with NNO blocking sites derived from several N-substituted diamines and aromatic mono aldehydes specifically salicylaldehyde or its analogues were focussed in this brief review. Total nine different Schiff base ligands (HL^1-HL^9) [20-28] have been used to prepare the complexes under consideration. **Scheme-I**



HL¹ [Ref. 20] **HL²** [Ref. 21] **HL³** [Ref. 22]

HL⁴ [Ref. 23] **HL⁵** [Ref. 24] **HL⁶** [Ref. 25]

HL⁷ [Ref. 26] **HL⁸** [Ref. 27] **HL⁹** [Ref. 28]

Scheme-I: Tridentate Schiff base ligands with NNO donor sites under consideration depicts the structures of tridentate NNO donor blocking Schiff base ligands.

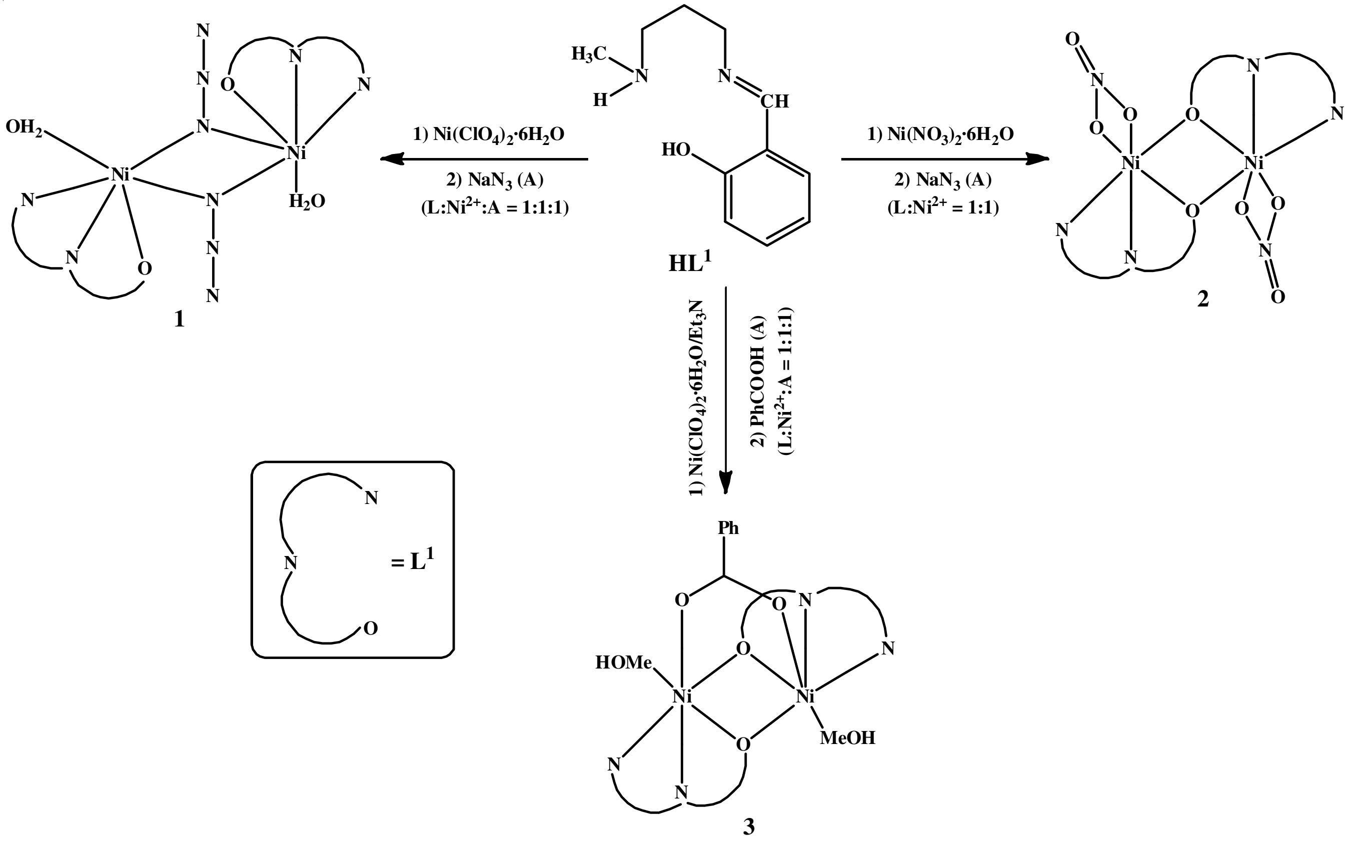
Structural features, magnetic properties and magnetostructural correlation of dinuclear Ni(II) complexes with tridentate Schiff base ligands with NNO chelator: This review primarily focuses on the dinuclear Ni(II) complexes of Schiff base ligands having NNO blocking sites and were supported by various polyatomic bridging co-ligands. The metal ion remains coordinately unsaturated unless the crystal field stabilization energy of the ligands is sufficiently high to stable the Ni(II) ion in a square planar configuration. This is because the tridentate ligand and counter anion balance the charge. Taking advantage of the phenoxido oxygen's bridging characteristics, those of anion or both, is highly advantageous in this scenario [20]. Numerous studies revealed that even a minute change in the stereoelectronic feature of the diammine and/or carbonyl results in considerable changes in the spatial orientation of the Ni(II) ion. Moreover in presence of a polyatomic bridging ligand along with the NNO donor Schiff base, the structure becomes further complicated. Therefore application of this phenomenon, *i.e.* NNO Schiff base ligands in combination with various polyatomic anions can be employed as an efficient tool for developing designed structural frameworks, which are capable of showing functionally vital magnetic coupling behaviour [29,30].

Dinuclear Ni(II) complexes of tridentate Schiff base ligands with NNO blocking sites based on N-substituted propanediamines: Under this category, the synthetic strategy, structural elucidation and magnetic properties of 19 dinuclear Ni(II) complexes of six different tridentate NNO donor Schiff base ligands derived from 1:1 condensation of N-substituted propanediamine with salicyldehyde or its analogues are discussed. The magnetostructural corroboration of the nickel(II) Schiff base complexes was also emphasized.

Synthesis of complexes 1-3: Three dinuclear nickel(II) complexes $[Ni_2L^1_2(N_3)_2(H_2O)_2]$ (**1**), $[Ni_2L^1_2(NO_3)_2]$ (**2**) and $[Ni_2L^1_2(O_2CPh)(CH_3OH)_2]ClO_4·0.5CH_3OH$ (**3**) were synthesized using a tridentate NNO donor Schiff base ligand HL^1 = (2-[(3-methylaminopropylimino)methyl]phenol) in conjugation with monoanionic coligands N_3^-, NO_3^- and $PhCOO^-$ [20]. A methanolic solution of $Ni(ClO_4)_2·6H_2O$ was reacted with Schiff base ligand HL^1 followed by addition of sodium azide solution in aqueous methanolic mixture (for **1**), benzoic acid (for **3**), to create complexes **1** and **3**. Nickel nitrate solution and the ligand (HL^1) were mixed in a equimolar proportion to obtain complex **2**. **Scheme-II** illustrates the synthetic pathway of complexes **1-3**.

Structural aspects and magnetic characterization of complexes 1-3: Complex $[Ni_2L^1_2(N_3)_2(H_2O)_2]$ (**1**) is a centrosymmetric dimer in which two azido ligands linked the metal centers in end on manner. Three chelating donor atoms of the Schiff base ligand, two nitrogen atoms from the two bridging azides and an oxygen atom from the terminal water molecule produce the deformed octahedral surrounding the nickel(II) centre. The Ni-N(azido)-Ni bond angles of 101.61(15)° and the Ni-N(azido) bond distances of 2.096(3) and 2.143(3) Å characterize the double azido bridged Ni_2N_2 asymmetric core of complex **1**.

$[Ni_2L^1_2(NO_3)_2]$ (**2**) has a distinct centro-symmetric dimeric crystal structure. A bidentate nitrate anion, the deprotonated



Scheme-II: Synthetic route of the complexes **1-3**

chelating Schiff base ligand and a phenoxido oxygen atom from the second Schiff base together combine to generate a distorted octahedral environment for each of the two nickel atoms. The double phenoxido bridge connecting the two Ni(II) ions makes the Ni_2O_2 unit a little asymmetric because each Ni(II) ion is closer to its own phenoxido oxygen atom (Ni-O = 2.009(2) Å) than to the phenoxido oxygen atom of another Schiff base (Ni-O = 2.070(3) Å). The distance (3.119 Å) that separates two Ni atoms and the Ni-O(phenoxido)-Ni angle is 99.75(10)°.

$[Ni_2L^1_2(O_2CPh)(CH_3OH)_2]ClO_4\cdot 0.5CH_3OH$ (**3**) is a dinuclear Ni(II) complex which is triply bridged and has two *syn-syn* bidentate benzoate bridges in addition to di-μ_2-phenoxido-bridges. A discrete dinuclear cationic unit $[Ni_2L^1_2\text{-}(O_2CPh)\text{-}(CH_3OH)_2]^+$ and a solvent molecule comprising CH_3OH and ClO_4^- acting as a counter anion make up the crystal structure of **3**. Two Ni(II) atoms are joined by two μ_2-phenoxido oxygen atoms of the Schiff-base ligands and two bridging oxygen atoms of a bidentate benzoate ligand to create the dinuclear unit. Two phenoxido oxygen atoms and the amino and imino nitrogen atoms constitute the basal plane and the two axial position are occupied by one oxygen atom from a bridging benzoate ligand and an oxygen atom from a coordinated methanol. Thus, the octahedral coordination of the two equivalent nickel atoms becomes satisfied. The double phenoxido bridged Ni_2O_2 core is slightly asymmetric with each Ni(II) ion being nearer to its own phenoxido oxygen atom [Ni-O = 2.049(3) Å] than to the phenoxido oxygen atom of the symmetry related Schiff base (Ni-O =2.114(3) Å). Two identical bridging $Ni\text{-}O_{(phenoxido)}$ -Ni angles are 96.60(12)°.

The magnetic study discloses that two Ni(II) centers in complex **1** are ferromagnetically united along with antiferromagnetic interdimer interactions. The complex exhibits both antiferromagnetic (J = -0.513(3) cm^{-1}) and ferromagnetic (J = 23.5(3) cm^{-1}). As the temperature is lowered, the dimer exhibits an increase in χ_MT, peaking at approximately 32 K with 2.8 emu K mol^{-1}. Below this point, χ_MT drops quickly, reaching a value of about 0.65 emu K mol^{-1} at 2K.

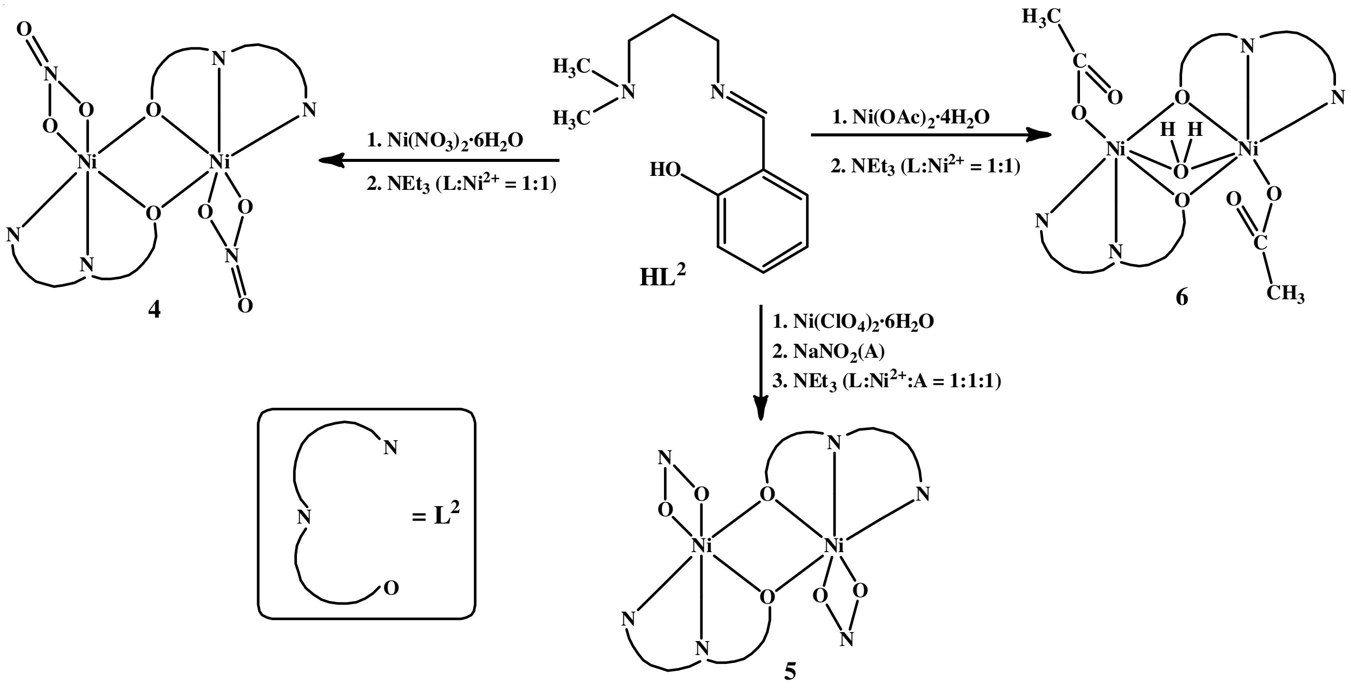
Complexes **2** and **3** exhibit the magnetic behaviour that suggests the presence of antiferromagnetic exchange contacts within the Ni(II) dimers. Within this Ni(II) dimer, complex **2** exhibits an antiferromagnetic exchange interaction with J = -24.27(6) cm^{-1}. Complex **3** exhibits antiferromagnetic magnetic behaviour with a J = -16.48(4) cm^{-1}. The measured coupling (J = -16.48 cm^{-1}) of complex **3** is higher than predicted, suggesting that the complex's extra *syn-syn* carboxylato bridge is also influencing the complex's overall magnetic coupling. Complex **3** is anticipated to have an extra antiferromagnetic contribution, consistent with the experimental findings, as *syn-syn* bridging carboxylate are known to assist antiferromagnetism [30].

Magnetostructural correlation of complexes 1-3: The ferromagnetic value (J = +23.5 cm^{-1}) of complex **1** exchange falls between +20.1 to +47.6 cm^{-1}, which is the range for Ni(II) complexes with double $\mu_{1,1}$-N_3 bridges. Only a rough magnetostructural link with the Ni-N-Ni bond angle has been found, despite numerous attempts to correlate the magnetic exchange with bridging Ni-N-Ni bond angles and Ni-N distances [1]. Using DFT calculations on several metal complexes with double $\mu_{1,1}$-N_3 bridges, Ruiz *et al.* [30] demonstrated a slight influence of the J value on the Ni-N-Ni bond angle. The magnetostructural correlations developed for phenoxido-bridged Ni(II) complexes, primarily from the Ni-O-Ni bond angle, are consistent with the antiferromagnetic coupling observed in complexes **2** and **3** (J = -24.27 and -16.48 cm^{-1}, respectively) with the Ni-O-Ni bond angles 99.75(10) and 96.60(12)°, respectively. These correlations have unambiguously demonstrated that ferromagnetic coupling weakens and turns antiferromagnetic at Ni-O-Ni angle of about 97-98°. Complex **3**'s experimental coupling (-16.48 cm^{-1}) is higher than anticipated, suggesting that the complex's extra carboxylato bridge (*syn-syn*) enhanced the antiferromagnetic contribution.

Synthesis of complexes 4-6: Synthetic stategies, crystal structure and magnetic behaviour of three di-phenoxido bridged dinickel(II) complexes, $[Ni_2L^2_2(NO_3)_2]$ (**4**), $[Ni_2L^2_2(NO_2)_2]$ (**5**) and $[Ni_2L^2_2(CH_3COO)_2(H_2O)]\cdot H_2O$ (**6**) were reported in the literature [31]. The Schiff base ligand HL^2 (2-[(3-dimethylaminopropylimino)methyl]phenol) reacted with methanolic solution of nickel(II) nitrate and nickel(II) acetate in equimolar ratio to obtain complexes **4** and **6**, respectively. Complex **5** was synthesized by the reaction of $Ni(ClO_4)_2\cdot 6H_2O$ and the Schiff base ligand (HL^2) in methanol medium followed by adding $NaNO_2$ solution. Equimolar quantity of NEt_3 was added for all three compounds to deprotonate the Schiff base. The synthetic pathway of complexes **4-6** is shown in **Scheme-III**.

Structural exposition and magnetic properties of complexes 4-6: The X-ray structures of both complexes **4** and **5** consist of di-μ_2-phenoxido bridged dimeric units of formula $[Ni_2L^2_2(NO_3)_2]$ (**4**) and $[Ni_2L^2_2(NO_2)_2]$ (**5**) with centre of symmetry. The nickel atoms are six-coordinated and situated in a highly deformed octahedral context in both complexes. Furthermore, each metal centre is coordinated *via* 2° amine nitrogen atom, imine nitrogen and phenoxido oxygen together with a μ_2-phenoxido O atom from the another Schiff base ligand along with bidentate chelating nitrate. The Ni_2O_2 core is slightly asymmetric as is typically observed in this sort of double oxido-bridged Ni(II) dimers [32], since each Ni(II) ion is closer to the chelated L^2 phenoxido oxygen atom than that is to another identical Schiff base moiety. The bridging angles of $Ni\text{-}O_{(phenoxido)}$-Ni are 99.31(8) and 100.01(7)° for complexes **4** and **5**, respectively.

$[Ni_2L^2_2(H_2O)(CH_3COO)_2]\cdot H_2O$ (**6**) consists of a isolated dinuclear core which is created by two nickel atoms, connected by one bridging H_2O molecule and two μ_2-phenoxido oxygen atoms. The six-coordination of each nickel centre is completed by the three donor atoms of Schiff base, another bridging phenoxido oxygen atom, one bridging water molecule and the carboxylate oxygen atom from terminal acetate ion. The Ni-Ni distance becomes 2.872(1) Å, significantly smaller than that of complexes **4** and **5** (3.124 and 3.156 Å) and other comparable diphenoxido bridged dinuclear nickel(II) complexes [33,34]. The two phenoxido bridging angles are 86.30(11)° and 87.18(10)°, respectively and the water bridge angle is of 86.71(12)°. The $Ni\text{-}O_{(water)}$ bonds ranging from 2.09-2.25Å as good as other previously accounted H_2O-bridged dinuclear Ni(II) compounds [29,35].



Scheme-III: Synthetic strategy of complexes **4-6**

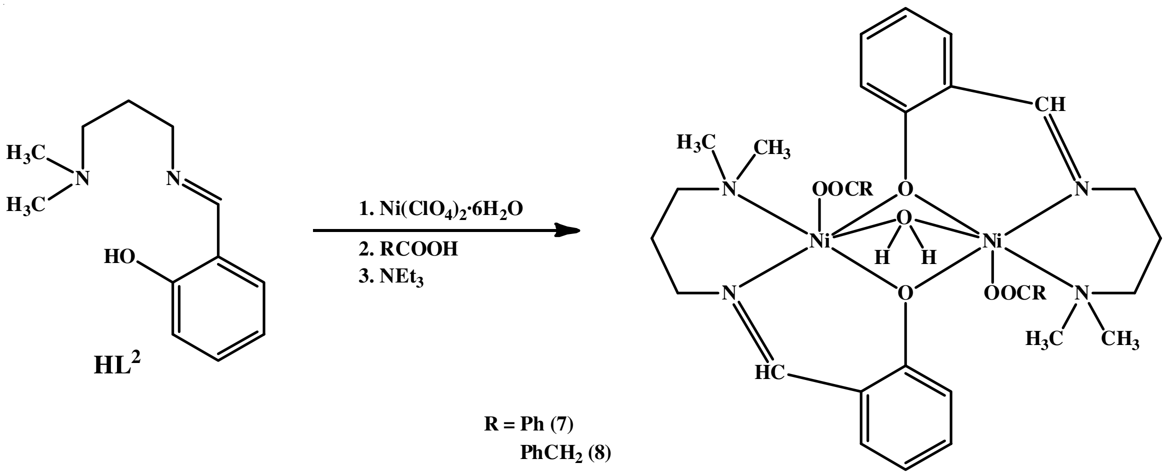
The $\chi_M T$ values of complexes **4-6** range from around 2.3 to 2.4 $cm^3K\ mol^{-1}$, which is consistent with the predicted value for two noninteracting Ni(II) S = 1 ions (2.0 $cm^3\ Kmol^{-1}$, g = 2). When the temperature is lowered to 2 K, complexes **4** and **5** exhibit very similar behaviour: $\chi_M T$ displays a gradual decrease at higher temperatures and a sharp decrease when the temperature is lowered further to values extremely close to zero. Complex **6** behaves differently: $\chi_M T$ progressively rises to a maximum value of 3.45 $cm^3\ Kmol^{-1}$at 15 K followed by a sharp decline to 2.94 $cm^3\ Kmol^{-1}$at 2 K. These findings show that while complex **6** is a ferromagnetic substance, complexes **4** and **5** present an antiferromagnetic coupling inside the dimer. The parameters *viz.* $J = -20.34(5)\ cm^{-1}$, g = 2.24(9) (for **4**) and $J = -25.25(4)\ cm^{-1}$, g = 2.27(8) (for **5**) optimized the data effectively. For compound **6**, the limiting values for $J = 19.11(9)\ cm^{-1}$ and g = 2.217(5).

Magnetostructural correlation of complexes 4-6: The two di-phenoxido bridged Ni(II) dimers **4** and **5** are antiferromagnetically connected as predicted by the Ni-O-Ni bridging angles [99.31(8)°, 100.01(7)°], according to the magnetic investigation. Nonetheless, the triply bridged complex **6** is ferromagnetic due to its reduced bridging angles [86.71(12)°, 86.30(11)° and 87.18(10)°]. DFT calculations, which are a useful tool for comprehending the complexes' magnetic interaction pathways, supported the overall experimental magnetic behaviour of the three complexes **4-6**. In dinuclear nickel complexes with either μ_2-phenoxido or both μ_2-water and μ_2-phenoxido bridges, the dependence of *J* value on the M-M spacing and bond angles subtended at the bridging atoms can be inferred through combined DFT calculations and magnetic studies.

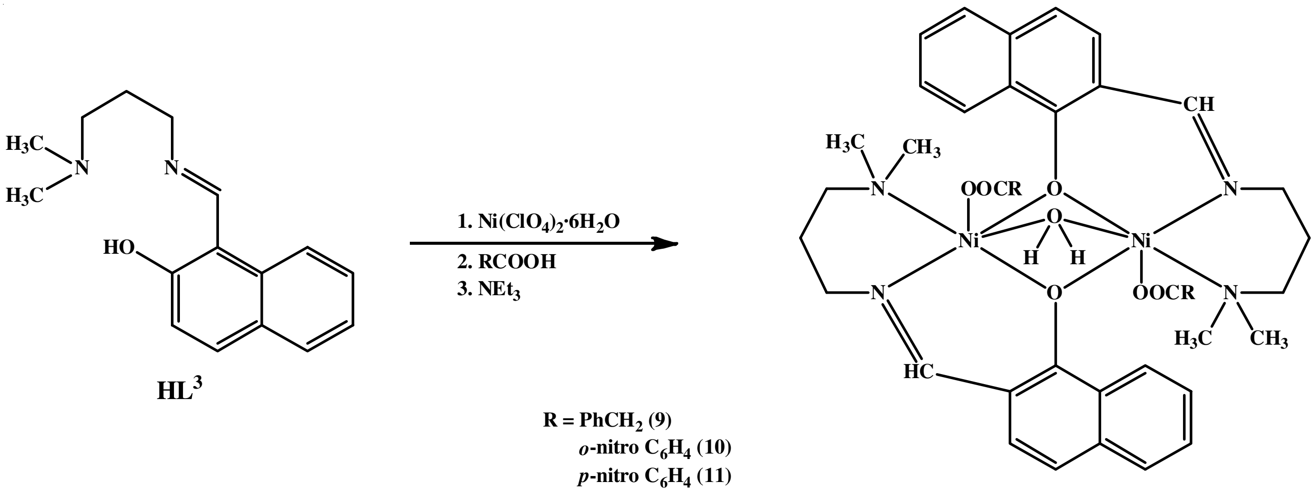
Synthesis of complexes 7-11: Five similar water bridging dinuclear nickel(II) complexes $[Ni_2L^2_2(PhCOO)_2(H_2O)]$ (**7**) [21], $[Ni_2L^2_2(PhCH_2COO)_2(H_2O)]$ (**8**) [21], $[Ni_2L^3_2(o\text{-}(NO_2)C_6H_4COO)_2(H_2O)]$ (**9**) [36], $[Ni_2L^3_2(p\text{-}(NO_2)C_6H_4COO)_2(H_2O)]·0.5CH_3OH$ (**10**) [36] and $[Ni_2L^3_2(PhCH_2COO)_2(H_2O)]$ (**11**) [22], were synthesized employing different carboxylates as mono-anionic coligands in combination with two tridentate NNO chelator Schiff base ligands (HL^2 and HL^3). Simply enabling Schiff base ligand (HL^2) to react with $Ni(ClO_4)_2·6H_2O$ in a CH_3OH medium and then adding benzoic acid (for **7**) or phenyl acetic acid (for **8**) in equimolar proportion was all that to synthesize the complexes. Triethylamine was added in an equimolar amount to deprotonate the Schiff bases and corresponding carboxylic acids. **Scheme-IV** displays the synthetic pathway for complexes **7** and **8**.

Similarly complexes **9**, **10** and **11** were obtained by the reaction of $Ni(ClO_4)_2$ with another tridentate Schiff base ligand (1-[(3-dimethylamino-propylimino)-methyl]-naphthalen-2-ol) (HL^3) in presence of phenyl acetic acid (for **9**), *o*-nitro benzoic acid (for **10**) and *p*-nitro benzoic acid (for **11**). The synthetic route for complexes **9-11** is shown in **Scheme-V**.

Structure description and exploration of magnetic properties of complexes 7-11: The molecular structures of complexes **7** and **8** are very similar to that of **6** except the terminally coordinated carboxylate groups. The two phenoxido bridging angles of complexes **7** and **8** are in the range 85.42-87.32° and the water bridging angle is 85.83° in 7 and 87.04° in **8**. As revealed from X-ray crystallography the molecular structures of complexes $[Ni_2L^3_2(o\text{-}(NO_2)C_6H_4COO)_2(H_2O)]$ (**9**), $[Ni_2L^3_2(p\text{-}(NO_2)C_6H_4COO)_2(H_2O)]·0.5CH_3OH$ (**10**) and $[Ni_2L^3_2(PhCH_2COO)_2(H_2O)]$ (**11**) are similar. The dinuclear unit of the three complexes is formed by two independent nickel atoms bridged by one water molecule and two μ_2-phenoxido oxygen atoms. The basic difference between the three structures is that the terminally coordinated carboxylate group is different phenylacetate in complex **9**, *p*-nitrobenzoate in



Scheme-IV: Synthetic protocol of complexes **7-8**



Scheme-V: Synthetic methodology of complexes **9-11**

complex **10** and *o*-nitrobenzoate in complex **11**. Each of the two metal centers are positioned in a deformed octahedral environment, being coordinated to the three donor atoms (N,N,O) of the Schiff base ligand along with bridging phenoxido oxygen atom of the second Schiff base ligand. The hexacoordination is fulfilled by the terminally coordinated monodentate carboxylate ions and the oxygen atom of the bridging water molecule. The phenoxido Ni–O–Ni bridging angles ranges from 85.06° to 86.9° and Ni–$O_{(water)}$–Ni water bridging angle falls within the range 85.26° to 88.12°. The Ni-$O_{(water)}$ bond distances are in the range 2.09-2.25 Å.

A moderate ferromagnetic exchange interaction is revealed by the variable-temperature magnetic studies of complexes **7** and **8**. Complexes **7** and **8** behave extremely similarly when the temperature is lowered, as a result of cooling, $\chi_M T$ gradually rises to a maximum value of 3.410 and 3.431 cm^{-1} mol^{-1} K at 9 and 16 K, respectively. Thereafter, it sharply declines to 2.952 and 2.527 cm^{-1} mol^{-1} K, respectively, at 1.8 K. Where the best fitting parameters were for complex **7**, J = 11.1(2) cm^{-1}, g = 2.176(3) and for complex **8**, J = 10.9(2) cm^{-1}, g = 2.195(2).

Complexes **9** through **11** underwent temperature-dependent molar susceptibility tests, with temperatures ranging from 2 to 300 K. The magnetic behaviour of complexes **9**, **10** and **11** exhibit remarkably comparable behaviour suggesting the presence of antiferromagnetic interdimer contacts and/or ZFS of the resultant S = 2 spin ground state in addition to ferromagnetic exchange interactions inside the Ni(II) dimer. At 300 K, the $\chi_M T$ value is 2.65 emu mol^{-1} cm^3 (for **9**), 2.78 emu mol^{-1} cm^3 (for **10**) and 2.92 emu mol^{-1} cm^3 (for **11**). This value is higher than expected when accounting for the orbital contribution (g = 2) and the contribution of two S = 1 spin centres. As the temperature decreases, $\chi_M T$ rises and reaches a maximum of 3.55 emu mol^{-1} cm^3 at about 17 K (for **9**) 3.84 cm^3 mol^{-1} K at around 14 K for complex **10** and 3.81 cm^3 mol^{-1} K at around 10 K for complex **11**, a value near to the expected for a S = 2 ground state suggesting ferromagnetic coupling between the two S = 1 centres. The magnetic parameters that suit best for g = 2.21, J = 26.20 cm^{-1}, |D| = 0.17 cm^{-1}, (**9**) J = 25.4 cm^{-1}, g = 2.27, |D| = 3.20 cm^{-1} (**10**) and J = 28.1 cm^{-1}, g = 2.23, |D| =2.80 cm^{-1} (**11**).

Magnetostructural correlation of complexes 7-11: Special emphasis must be placed on the role of additional water bridge in rendering the exchange coupling ferromagnetic in this instance. The Ni-Ni distance reduces as a result of additional water bridge, according to a comparison of the structural properties of these triple spanned compounds with those of the only diphenoxido bridged species [33,34]. Consequently, shorter Ni-Ni distances result in lower average Ni-O-Ni angles, as does the average Ni-O-Ni bridging angle. To make the exchange coupling ferromagnetic, it may be generally expected that each additional bridge, aside from water, should likewise reduce the Ni-$O_{(phenoxido)}$-Ni angle to a value below the critical one in diphenoxido bridged complexes.

Synthesis of complex 12: $Ni(ClO_4)_2·6H_2O$ was constantly stirred with a tridentate Schiff base (1:1 condensation product of N,N-dimethyl-1,3-propanediamine and 2-hydroxy-1-napthaldehyde) followed by addition of triethylamine. Then, the resultant green solution was mixed with an aqueous solution of sodium dicyanamide. The filtrate was gradually evaporated, yielding block-shaped and intensely green single crystals of $[Ni_2L^3_2(N(CN)_2)_2(H_2O)]$ (**12**) (**Scheme-VI**) [22].

Structure description and magnetic coupling of complex 12: The structure of complex **12** is made up of double end-to-end dicyanamide bridges connecting two nickel atoms in the centrosymmetric dinuclear unit. Three donor atoms of Schiff base ligand in face coordination mode, two N atoms from the $\mu_{1,5}$ dicyanamide moities and one oxygen atom of the terminal water molecule are utilized to accomplish hexacoordination of each nickel atom. The range of the Ni-N lengths is 1.988(3)-2.117(3) Å. The Ni-$O_{(phenoxido)}$ bond distance is 1.956(3), but the Ni-$O_{(solvent)}$ bond distance is 2.412(7) Å, which suggests that the solvent water molecule has very poor coordination with Ni(II). An intermolecular N···H bonds are formed involving H atoms of the terminally coordinated H_2O and the N atom of the bridging dicyanamide group of neighboring molecule. These extended hydrogen bonding form a 2-D arrangement.

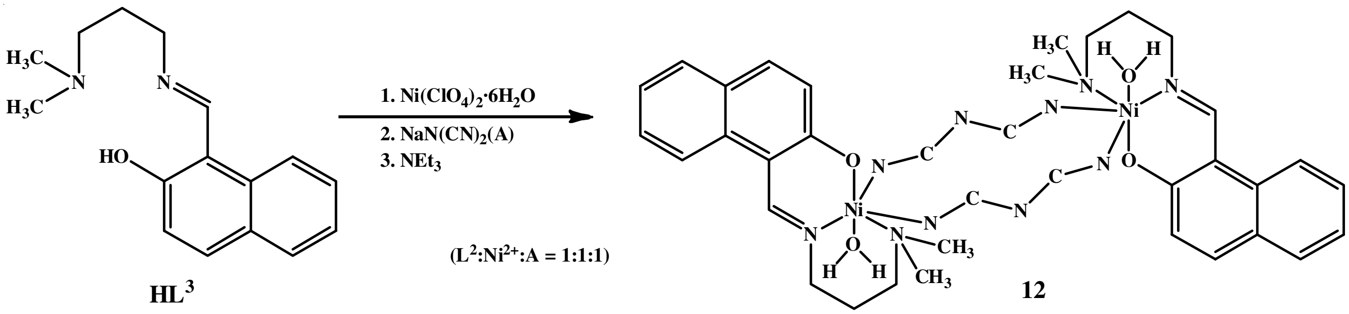
The molar magnetic susceptibility studies of complex **12** was conducted in the span of 2-300 K. The estimated $\chi_M T$ value of 2.0 emu mol^{-1} K for two uncoupled S = 1 spins at room temperature is extremely close to the observed value of 2.37 cm^3 mol^{-1} K. Up to 45 K, the $\chi_M T$ value was constant; after that, it rapidly dropped as the temperature was lowered, reaching a minima at around 0.75 emu mol^{-1} K at 2 K. If we take out the intermolecular interactions, $J = -1.90$ cm^{-1} and g = 2.18 were the best fits.

Magnetostructural correlation of complex 12: Complex **12** has a large Ni···Ni spacing of 7.341 Å as $\mu_{1,5}$-dicyanamide bridges occur between the two nickel atoms. In the majority of dicyanamide-containing complexes the metal-metal separation is bigger than 7.0 Å and demonstrate weak antiferromagnetism (J values varied from *ca.* -0.3 to -1.2 cm^{-1}) [37-40]. Nonetheless, a small number of specimens also show very weak ferromagnetic coupling (J values ranging from about +1.0 to +0.7 cm^{-1}). As a result, the magnetic coupling across the dicyanamide bridge is typically modest, but it is difficult to forecast whether the interactions would be ferromagnetic or antiferromagnetic because there are currently no effective theoretical models available to analyse these systems' magneto-structural relationships.

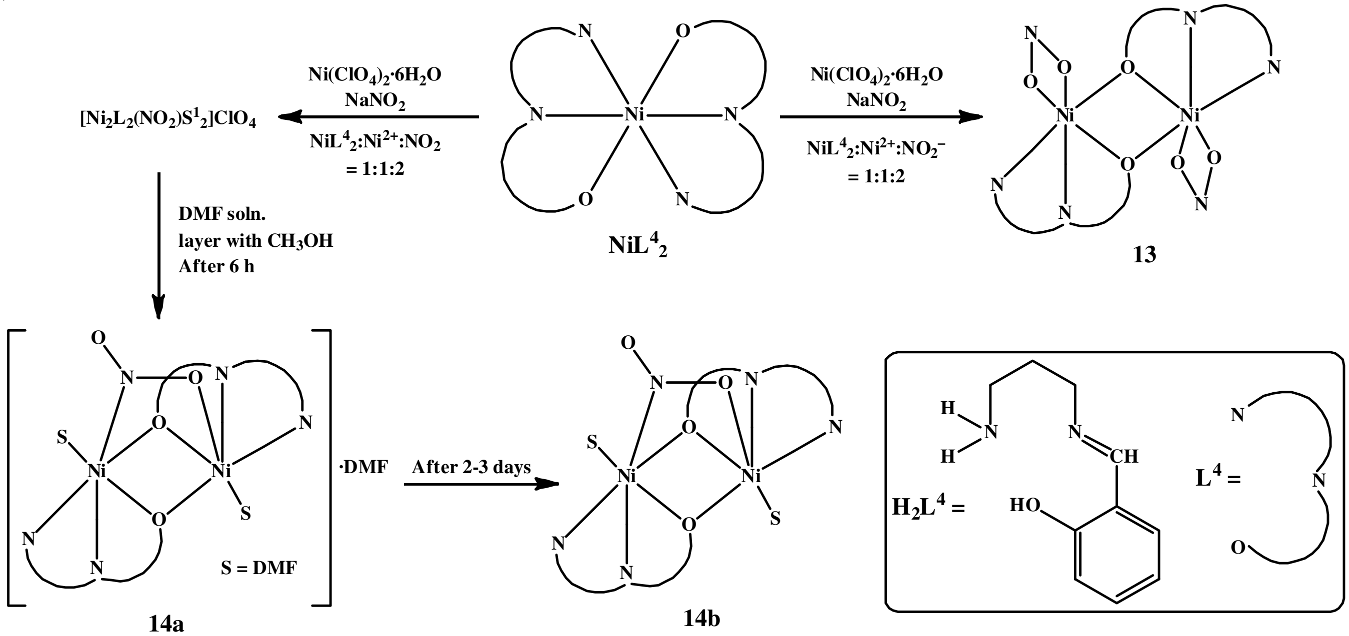
Synthesis of complexes 13, 14a and 14b: With a single condensed tridentate NNO donor Schiff base ligand (2-[(3-aminopropylimino)methyl]phenol), three nickel(II) complexes $[Ni_2L^4(NO_2)_2]·CH_2Cl_2·C_2H_5OH·2H_2O$ (**13**), $[Ni_2L^4_2(DMF)_2(\mu\text{-}NO_2)]ClO_4·DMF$ (**14a**), $[Ni_2L^4_2(DMF)_2(\mu\text{-}NO_2)]ClO_4$ (**14b**) have been reported [23]. Metastable species **14a** first manifests as a kinetically regulated result during the crystallization process. When it comes into contact with the solution, it becomes the thermodynamically preferred product, **14b**, which then undergoes redissolution and recrystallization.

Structural elucidation and magnetic studies of complexes 13, 14a and 14b: The dinuclear di-μ_2-phenoxido bridged species in complex **13** is characterized by the chelating co-ligand function of nitrite ion. The Ni–$O_{(phenoxido)}$ bond is appreciably longer at 2.081(5) Å than the Ni–$O_{(phenoxido)}$ bonded to the other Schiff base ligand making the Ni_2O_2 unit unsymmetrical with the Ni–O–Ni angle is 98.28(19)º. The other two complexes, **14a** and **14b**, are made up of dinuclear entities; however, in these compounds, there is also a bridging nitrito group (1kO: 2kN) along with two μ_2-phenoxido bridges, the only difference between **14a** and **14b**'s molecular structures is that **14a** has one extra solvated DMF molecule (**Scheme-VII**) [23].

Complexes **13**, **14a** and **14b** underwent magnetic susceptibility tests at temperatures between 1.8 and 300 K. The room temperature $\chi_M T$ values of compounds **13**, **14a** and **14b** are around 2.3, 2.3 and 2.2 emu mol^{-1} K, respectively. These values are consistent with the anticipated value of 2.0 emu mol^{-1} K for two non-interacting Ni(II) S = 1 ions. Compounds **13**, **14a** and **14b** behave extremely similarly when the temperature is lowered. At elevated temperatures, $\chi_M T$ exhibits a gradual decrease; however, when the temperature drops more, the decline becomes more noticeable, reaching values that are extremely near to zero at 1.8 K. The magnetic behaviour suggests that there are antiferromagnetic exchange contacts among the three chemicals in the Ni(II) dimer. The basic parameter values that suits the best are: for complex **13**, $J = -5.26$ cm^{-1}, g = 2.19, D = 2.67 cm^{-1}; for complex **14a** $J = -11.45$ cm^{-1}, g = 2.21, D =



Scheme-VI: Synthetic pathway of complex **12**



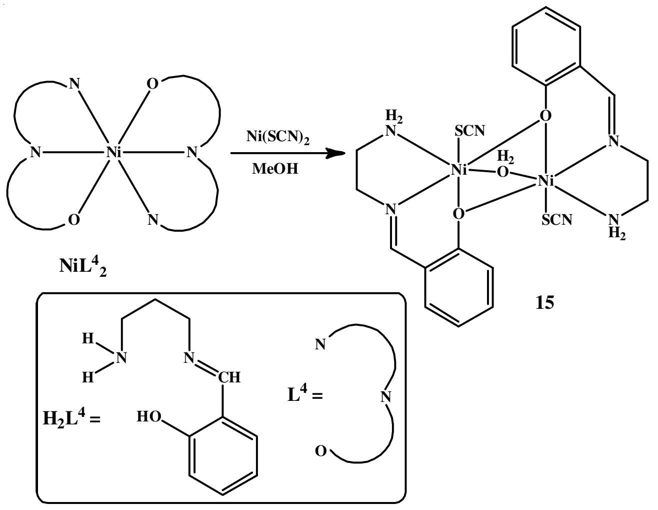
Scheme-VII: Synthesis of complexes **13**, **14a** and **14b**

7.94 cm^{-1} and for complex **14b**, J = -10.66 cm^{-1}, g = 2.19 and D = 8.89 cm^{-1}.

Magnetostructural correlation of complexes 13, 14a and 14b: The angle Ni–O–Ni that unites the Ni^{2+} ions in complexes **14a** and **14b** (95.17 and 95.02°) suggests that this bridge contributes more ferromagnetically. The resulting coupling has a reduced J value (J = -5.99 cm^{-1}), but it is still antiferromagnetic and dominated by the 1kN:2kO nitrite bridging. The final value of the magnetic coupling constants (J), which controls the observed magnetic behaviours, may have competing +ve and -ve counterpart in case of hetero-bridged systems. This could lead to counter-complementary outcomes between the different ligands.

Synthesis of complex 15: One more dinuclear di-μ_2-phenoxido bridged Ni(II) complex $[Ni_2(L^4)_2(H_2O)(NCS)_2]\cdot 3H_2O$ (**15**) was reported with an additional water bridge [41]. By reacting Ni(II) nitrate, salicylaldehyde and 1,3-propanediamine, the monocondensed ligand N-(3-aminopropyl)salicylaldimine (L^4) was created as [NiL$^4_2$]. In methanolic solution, [NiL$^4_2$] easily interacted with Ni(SCN)$_2$ in a equimolar ratio to form the μ_2-phenoxido and H$_2$O-bridged complex $[Ni_2(L^4)_2(H_2O)(NCS)_2]\cdot 3H_2O$ (**15**) (**Scheme-VIII**).

Structural aspects and magnetic behaviour of complex 15: In dimeric unit of complex **15**, two Ni(II) atoms are bridged by the H$_2$O molecule and the two μ_2-phenoxido groups of the respective Schiff-base. The octahedral surroundings of the two corresponding nickel atoms are deformed. The two nitrogen and two oxygen atoms of the bridging phenoxido ligands combine to produce the basal plane Ni$_2$N$_2$O$_2$. The axial locations are occupied by the oxygen atom of the bridging aqua ligand and the nitrogen atom of the thiocyanato terminal ligand. The Ni–O$_{(water)}$–Ni bridge angle is 82.5(5)°, while two Ni–O$_{(phenoxido)}$–Ni bridge angles are 91.5(4)°. An extended hydrogen bonding is produced by connecting N atom of the SCN$^-$ ligand with both bridging H$_2$O molecule and H$_2$O molecules outside the coordination sphere.



Scheme-VIII: Synthetic strategy of complex **15**

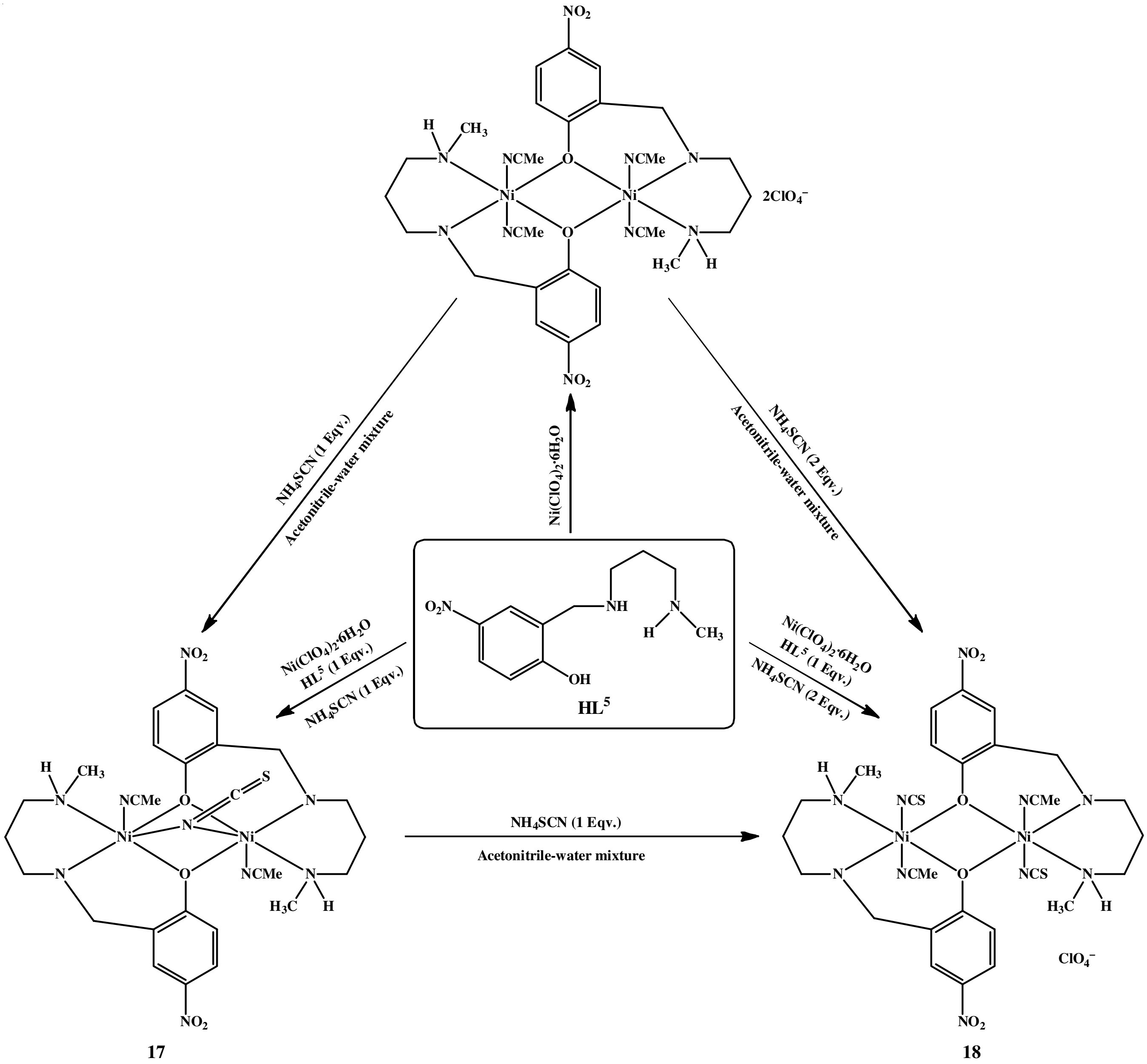
In complex **15**, the χ_MT values exhibit a progressive rise from 2.70 cm^{-1} mol^{-1} K at ambient temperature to 3.25 cm^{-1} mol^{-1} K at 6 K and then a decrease at a lower temperature. A system with dominating intramolecular ferromagnetic exchange coupling would behave in this way. The parameters that fit the data the best were J = 3.1(1) cm^{-1}, g = 2.29(1) and D = 1.8(1) cm^{-1}, where D is the ZFS parameter.

Magnetostructural correlation of complex 15: In Ni(II) dimmers J value is in direct relationship with Ni–O–Ni bridge angles or Ni···Ni spacing and this correlation was established by Nanda *et al.* [33]. As a result, the coupling is ferromagnetic with J values of about 10 cm^{-1} for Ni–O–Ni angles around 90°. The phenoxido and the H$_2$O are two distinct bridges that are used to explain the magnetic properties of complex **15**, which have a noncentrosymmetric structure and a deformed octahedral geometry surrounding the Ni^{2+} ions. The Ni centers are 2.953(4) Å apart and the Ni–O$_{(phenoxido)}$–Ni bridge angle =

91.5(4)° and the Ni–$O_{(water)}$–Ni bridge angle is 82.2(4)°. If the two bridging angles are taken into consideration then it is for sure that there could be ferromagnetic exchange through the two kinds of bridges.

Synthesis of complexes 16-18: A nickel(II) complex $[Ni_2L^5_2(CH_3CN)_4](ClO_4)_2{\cdot}2CH_3CN]$ (**16**) was synthesized employing the reduced Schiff base ligand (HL^5), 2-[(3-methylamino-propylamino)methyl]-4-nitrophenol as a tridentate NNO donor $Ni(ClO_4)_2{\cdot}6H_2O$. Complex $[Ni_2L^5_2(CH_3CN)_4](ClO_4)_2{\cdot}2CH_3CN]$ (**16**) has generated two more Ni(II) complexes, $[Ni_2L^5_2(\mu_{1,1}\text{-}NCS)(CH_3CN)_2](ClO_4){\cdot}CH_3CN]$ (**17**) and $[Ni_2L^5_2(NCS)_2(CH_3CN)_2]$ (**18**) through reaction with one and two equivalents of NH_4SCN, respectively [24]. It is fascinating to observe that complex **18** has all been produced by adding 1 equiv. NH_4SCN to the solution of complex **17**. The synthetic route of complexes **16-18** is depicted in **Scheme-IX**.

Structural description and elaboration of magnetic coupling of complexes 16-18: Ni(II) complexes $[Ni_2L^5_2(CH_3CN)_4]$-$(ClO_4)_2{\cdot}2CH_3CN]$ (**16**) and $[Ni_2L^5_2(NCS)_2(CH_3CN)_2]$ (**17**) have extremely similar dinuclear structures. A diphenoxido bridge connects the Ni(II) ions in both of them but in complex **17** an extra $\mu_{1,1}$-NCS bridge is also present in addition to the diphenoxido bridges. Two Ni(II) atoms make up the binuclear core of complex **16**, which is connected by diphenoxido oxygen atoms at a bridging angle of 102.41(11)°. Three donor centers of chelating Schiff base ligand and one phenoxido oxygen of the other Schiff base constitute the basal plane of each nickel atoms with usual bond distances [26,42,43]. The hexa-coordination of nickel centres is fulfilled by two axial acetonitrile solvent molecule to each nickel atom. Two separate perchlorate molecules neutralize the charge on the complex.



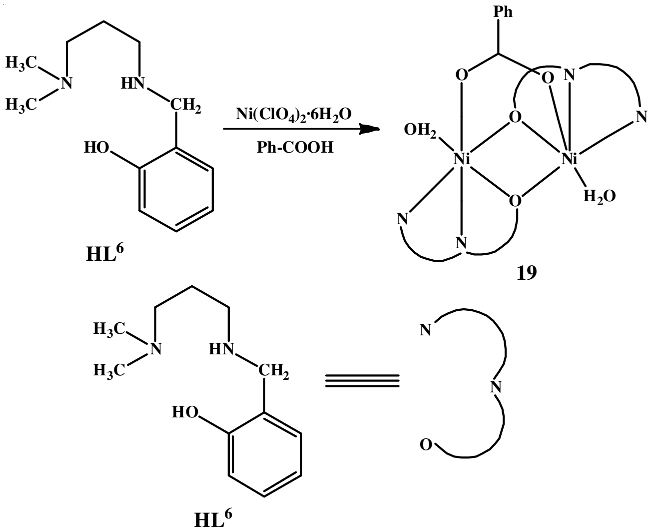
Scheme-IX: Synthetic procedure of complex **16-18**

The Ni_2O_2 core of complex **17** is comparable to that of complex **16**. The primary distinction, though, is that a thiocyanate anion takes the place of one axial CH_3CN creating an extra $\mu_{1,1}$-NCS bridge between two Ni(II) centres and forcing them to approach one another with a shorter distance of 2.958 Å than 3.244 Å and 3.267 Å in complexes **16** and **18**, respectively. In comparison to complexes **16** (102.41(11)°) and **18** (102.42 (14)°), the shorter Ni–Ni distance causes the $Ni–O_{(phenoxido)}–Ni$ bond angles (Ni1–O–Ni, 90.90(14)° and 91.65(17)°) to drop [31,36]. The Schiff base ligand coordinates each Ni(II) ion in its distorted octahedral environment through 2° amine N atoms and phenoxido O atoms, respectively, with standard bond lengths. The two nickel centres' octahedral environment is completed by the coordinated acetonitrile moieties and the bridging thiocyanate (NCS^-). The discrete centrosymmetric dimeric core of complex **18** is likewise extremely similar to that of complex **16**, which is made up of two Ni(II) atoms separated by diphenoxido oxygen atoms. Two NCS^- ions have replaced the two acetonitrile molecules that were coordinated to each Ni(II)'s axial location, which is the only difference. Two nickel atoms are separated by 3.267 Å and their phenoxido bridging angle is 102.42(14)°.

At normal temperature, the compounds exhibit χ_MT values of approximately 1.99 cm^3 K mol^{-1} for complex **16** and 2.20 cm^3 K mol^{-1} for complex **18**. These values are consistent with the value of a Ni^{II} dimer that is magnetically non-interacted, which is 2.0 cm^3 K mol^{-1} for g = 2 at 300 K. Nevertheless at room temperature, χ_MT value (2.42 cm^3 K mol^{-1}) is somewhat greater than the value predicted for uncoupled Ni(II) ions with g = 2 (2.0 cm^3 K mol^{-1}) in complex **17**. Complexes **16** and **18** exhibit a highly comparable variance. The following parameters result from the best fits: For complex **16**, J = -33.85 cm^{-1}, g = 2.11; J = +5.01 cm^{-1}, g = 2.18 for complex **17**; J = -23.43 cm^{-1}, g = 2.17, for complex **18**. The ferro- and antiferromagnetic behaviours of the three complexes are well-matched with their phenoxido bridging angles. It has been determined for the first time that the non-bridging axial co-ligands can significantly alter magnetic coupling: antiferromagnetic coupling is significantly stronger for a neutral solvent (CH_3CN) compared to an anionic ligand (NCS^-).

Magnetostructural correlation of complexes 16-18: Complexes **16** and **18** should demonstrate dominant antiferromagnetism with J= –33.85 cm^{-1} for **16** and –23.43 cm^{-1} for complex **18** as the bridging angles surpass the critical angle ~97° in both cases (102.41° for complex **16** and 102.42° for complex **18**). The difference between J values for complexes **16** and **18** can be explained with the help of DFT calculation that demonstrates the magnetic coupling is severely exaggerated by the substitution of a anionic ligand NCS^- (**16**) with a neutral acetonitrile (**18**) at the axial location of the Ni(II) atom. Whereas complex **17** shows ferromagnetic interaction with weakly positive J = 5.01 cm^{-1} based on the significant reduction in phenoxido bridging angles (91.27°) by the additional $\mu_{1,1}$-isocyanato bridge. As a result, the orbital counter complementary effect balances the antiferromagnetic input given by the NCS^- group and the ferromagnetic interaction through the phenoxido bridging groups. In fact, the ligand NCS^- increased the charge density in complex **18** as opposed to the neutral acetonitrile ligands in complex **16**, which causes a shift in the electronic component of magnetic coupling, resulting in the considerable reduction of the antiferromagnetic coupling.

Synthesis of complex 19: Another tridentate NNO donor reduced Schiff base ligand, HL^6 = ([(3-dimethylaminopropylamino)methyl]phenol], has been used to synthesize complex $[Ni_2L_2(O_2CPh)(H_2O)_2]ClO_4$ (**19**). In the presence of benzoic acid, nickel perchlorate combined with a reduced Schiff base ligand [(3-dimethylaminopropylamino)methyl]phenol (HL^6) (**Scheme-X**) [25].



Scheme-X: Synthetic modality of complex **19**

Structural facets and magnetic interactions of complex 19: Complex **19** is a di-μ_2-phenoxido-bridged dinuclear Ni(II) complex with a *syn-syn* benzoate bridge of molecular formula $[Ni_2L_2(O_2CPh)(H_2O]ClO_4$. In this species with two nickel centers, the metal atoms are linked by two bridging μ_2-phenoxido oxygen atoms of the Schiff-base ligand. The bridging bidentate benzoate oxygen, two amino nitrogen atoms of the Schiff base ligand and a terminally bonded water molecule complete the hexacoordinated octahedral core. The M-M separation is 3.11 Å whereas the Ni-O-Ni angle is 97.56°. The hydrogen atoms of the two coordinated water molecule are hydrogen bonded with the oxygen atom of noncoordinated perchlorate molecule. Weak hydrogen bonding between benzoate ligand, amine group and perchlorate anions forms a 2D porous sheet.

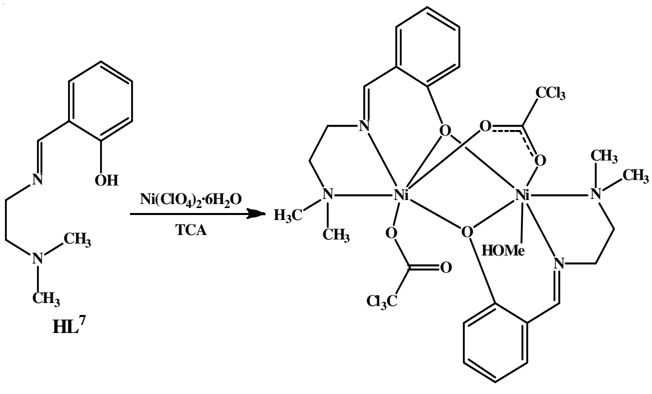
The magnetic analysis of complex **19** reveals the intradimer antiferromagnetic interactions (J = –5.65 cm^{-1}). The experimental χ_MT value at standard temperature is *ca.* 2.25 cm^3 K mol^{-1} and it indicates the presence of two magnetically noninteracting Ni(II) ions in the dimer. On lowering the temperature, χ_MT value gradually drops down; however, a swift fall is noted at near absolute zero temperature and we end with an observed value of 0.025 cm^3 K mol^{-1} at 1.8 K. The strongest antiferromagnetic correlation is observed with the specific values of g = 2.16, J = –5.65 cm^{-1}.

Magnetostructural correlation of complex 19: The molecular structure of complex **19** demonstrtes that one μ-$_{1,3}$-carboxylate bridge and two phenoxido bridges connect the

Ni(II) atoms to one another. The overall coupling constnt (J) is thought to be vector summation of three individual component from the three exchange pathways namely $\mu\text{-}_{1,3}$ carboxylate bridge and two phenoxido bridges. Consequently, a counter-complementarity effect is operating between the antiferro contribution of di-phenoxido bridging groups and the ferromagnetic interaction of the carboxylate group. Finally, the antiferromagnetic contribution predominates over the ferromagnetic one and producing $J = -5.65\ cm^{-1}$.

Dinuclear Ni(II) complexes of tridentate Schiff base having NNO donor sites based on N-substituted ethylenediamines: The structural variation and magnetic characteristics of five dinuclear Ni(II) complexes of tridentate NNO chelator Schiff bases originated from the condensation of respective N-substituted ethylenediamines with salicyldehyde or its derivatives in 1:1 molar ratio.

Synthesis of complex 20: One dinuclear Ni(II) complex $[(MeOH)(L^7)Ni(di\text{-}\mu\text{-}CCl_3CO_2)Ni(L^7)(CCl_3CO_2)]$ (**20**) was synthesized by mixing nickel perchlorate with the Schiff base $L^7 = \{(O\text{-})(C_6H_4CH{=}NCH_2CH_2NMe_3)\}$ [26] along with trichloroacetate (TCA) (**Scheme-XI**).



20

Scheme-XI: Synthetic strategy of the complex **20**

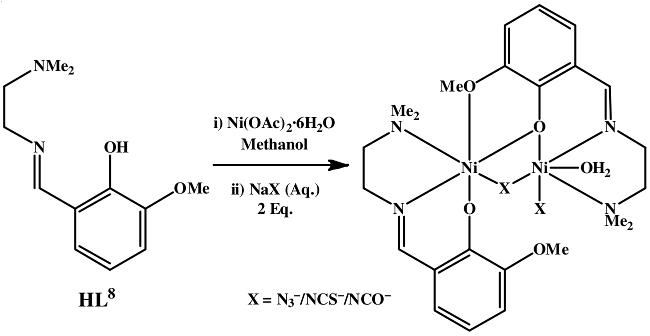
Structural elaboration and magnetic property of complex 20: In complex **20**, two nickel(II) centres are triply bridged in a *syn-syn* form by one trichloroacetate group and the two phenoxido groups of two Schiff bases. In addition, one metal centre contains a single trichloroacetate (TCA) group functioning as a monodentate terminal ligand, while another metal centre contains a single concatenated methanol group. A weak antiferromagnetic interaction is exhibited by complex **20**. At 300 K $\chi_M T = 2.62\ cm^3\ Kmol^{-1}$ and approaches to zero at low temperature. The most suitable parameters for complex **20** are $J = -11{:}98\ cm^{-1}$, g = 2:24.

Magnetostructural correlation of complex 20: A linear link between the exchange integral (J) and the phenoxido bridging angle has been inferred by Nanda *et al.* [33]. According to experimental findings, the rather weak antiferromagnetic interaction ($J = -11{:}98\ cm^{-1}$) appears to be a bit off from the average of the anticipated values when utilizing the prior relationship. This makes sense when the *syn-syn* conformation carboxylato bridge can facilitate more exchange pathways and boost the antiferromagnetic coupling.

Synthesis of complexes 21-23: The literature has documented three Ni(II) complexes *viz.* $[Ni(L^8)(\mu\text{-}_{1,1}\text{-}N_3)\text{-}Ni(L^8)(N_3)(OH_2)]\cdot H_2O$ (**21**), $\{[Ni(L^8)(\mu\text{-}_{1,1}\text{-}NCS)Ni(L^8)(NCS)\text{-}(OH_2)]\ [Ni(L^8)(\mu\text{-}CH_3COO)Ni(L^8)(NCS)(OH_2)]\}$ (**22A,22B**), $[Ni(L^8)(\mu\text{-}_{1,1}\text{-}NCO)Ni(L^8)(NCO)(OH_2)]\cdot H_2O$ (**23**) ($L^8 = Me_2N\text{-}(CH_2)_2NCHC_6H_3(O^-)(OCH_3)$). In these complexes end-to-end pseudohalide-bridged nickel(II) dimers, in which the metal atoms are bridged by azide, cyanate, thiocyanate or acetate groups in a $\mu\text{-}_{1,1}$ fashion, as well as by the μ_2-phenoxido oxygen atom, have been demonstrated [27].

$[Ni(L^8)(\mu_{1,1}\text{-}N_3)Ni(L^8)(N_3)(OH_2)]\cdot H_2O$ (**21**) was prepared by adding solid nickel acetate to the ligand in methanol. Sodium azide dissolved in minimum volume of water was added to the resulting mixture. After 2 days green coloured and rectangular shaped single crystals were obtained. For the synthesis of $[Ni(L^8)(\mu_{1,1}\text{-}NCS)Ni(L^8)(NCS)(OH_2)]\cdot H_2O$ (**22A,22B**) the same synthetic route was followed as that of complex **21** except for bridging ligand, instead of sodium azide an aqueous methanolic solution of sodium thiocyanate was added. After few days green, prismatic shaped crystals were observed.

Complex $[Ni(L^8)(\mu_{1,1}\text{-}NCO)Ni(L^8)(NCO)(OH_2)]\cdot H_2O$ (**23**) was obtained following almost identical process as of complexes **21** and **22**, the only difference was the bridging pseudohalide. Here, it was an aqueous solution of NaNCO used in place of azide, thiocyanate. Single crystal were isolated after 7 days from the filtrate (**Scheme-XII**). The colour and the shape of the crystals of complex **23** were quiet similar as that of complex **22**.



Scheme-XII: Synthetic protocol of the complex **21-23**

Structure description and magnetic characteristics of complexes 21-23: The unit of dinuclearity is $[Ni(L^8)(\mu_{1,1}\text{-}N_3)Ni(L^8)(N_3)(OH_2)]\cdot H_2O$ (**21**), which is composed of two Ni(II) atoms bridged by an $\mu_{1,1}$-azide group and a μ_2-phenoxido oxygen atom from the Schiff base. The methoxy oxygen atom of Schiff base and two nitrogen and one oxygen of the identical Schiff base ligand complete the octahedral coordination sphere of the Ni atom. The nitrogen atom of a axial azide ligand, two nitrogen atoms from the Schiff base and the water molecule occupy the residual positions of the distorted oh geometry of the Ni atom in a similar manner.

$\{[Ni(L^8)(\mu_{1,1}\text{-}NCS)Ni(L^8)(NCS)(OH_2)][Ni(L^8)(\mu_{1,1}\text{-}CH_3COO)Ni(L^8)(NCS)(OH_2)]\}$ (**22A,22B**) where $[Ni(L^8)(\mu_{1,1}\text{-}NCS)Ni(L^8)(NCS)(OH_2)]$ and $[Ni(L^8)(\mu\text{-}CH_3COO)Ni(L^8)(NCS)\text{-}(OH_2)]$ are the two separate binuclear units and (**22A**) (**22B**) comprise the asymmetric unit of complex **22**. The two identical pseudooctahedral Ni(II) centres in unit **22A** are held together by an thiocyanate-κN group in $\mu_{1,1}$ mode *via* a N atom and the μ_2-phenoxido oxygen atom of Schiff base ligand: one Ni centre has an N_4O_2 donor set while the other has a N_3O_3 donor set. In this case, two Schiff base molecules exhibit distinct behaviours. Two pseudooctahedral nickel centres in unit **22B** are bridged by the μ_2-phenolate O atom of Schiff base ligand and the CH_3COO^- ligand in *syn-syn* form using N_2O_4 and N_3O_3 donor sets, respectively.

The crystal structure of complex $[Ni(L^8)(\mu_{1,1}\text{-}NCO)Ni(L^8)(NCO)(OH_2)]\cdot H_2O]$ (**23**), is isostructural to that of complex **21**, except the pseudohalide OCN^- being replaced by N_3^- anion in complex **21**. In complex **23**, the Ni-O-Ni and Ni-$N_{(azido)}$-Ni bridging angles are 110.44(7) and 96.20(14)º, respectively.

Complex **21** exhibits significant ferromagnetic coupling, complex **23** has weak ferromagnetic behaviour and complex **22** exhibits extremely weak antiferromagnetic coupling. Both complexes **21** and **23** show usual ferromagnetic behaviours: effective magnetic moment increases with lowering temperature. At r.t $\chi_M T$ values are 2.60 and 2.42 $cm^3\ K\ mol^{-1}$ for complexes **21** and **23**, respectively and approaches a maxima of 3.42 $cm^3\ K\ mol^{-1}$ at 20 K for complex **21** and 2.52 $cm^3\ Kmol^{-1}$ at 17 K for complex **23**. After that, $\chi_M T$ slowly decreases and finally reaching values of 2.72 $cm^3\ Kmol^{-1}$ for complex **21** and 1.19 $cm^3\ Kmol^{-1}$ for complex **23** at 2 K. The limiting values are $J = +25.6\ cm^{-1}$, g= 2.20 and D = 6.8 cm^{-1}, for complex **21** and $J = +6.2\ cm^{-1}$, g = 2.19 and D = -0.22 cm^{-1}, for complex **23**.

Magnetostructural correlation of complexes 21-23: The type of bridging ligand and the interaction between the metal centres provide a satisfactory explanation for the variation in the size and sign of *J* observed for complexes **21-23**. The large (>100º) Ni-O-Ni angles in complexes **21-23** indicate that any exchange through phenoxido bridge is unlikely to be ferromagnetic; rather, based on the typical behaviour of dinuclear nickel(II) complexes and hydroxide [44] and alkoxide-bridged [45] compounds, one could expect this to contribute a weak antiferromagnetism. However, when the azido ligand bridges two metal ions in a $\mu_{1,1}$ way, it functions as a ferromagnetic coupler. Ferromagnetic interaction for complex **21** ($J = +39.0\ cm^{-1}$) is as expected as that of previously observed for di-$\mu_{1,1}$-bridged azido Ni(II) dimmer [46].

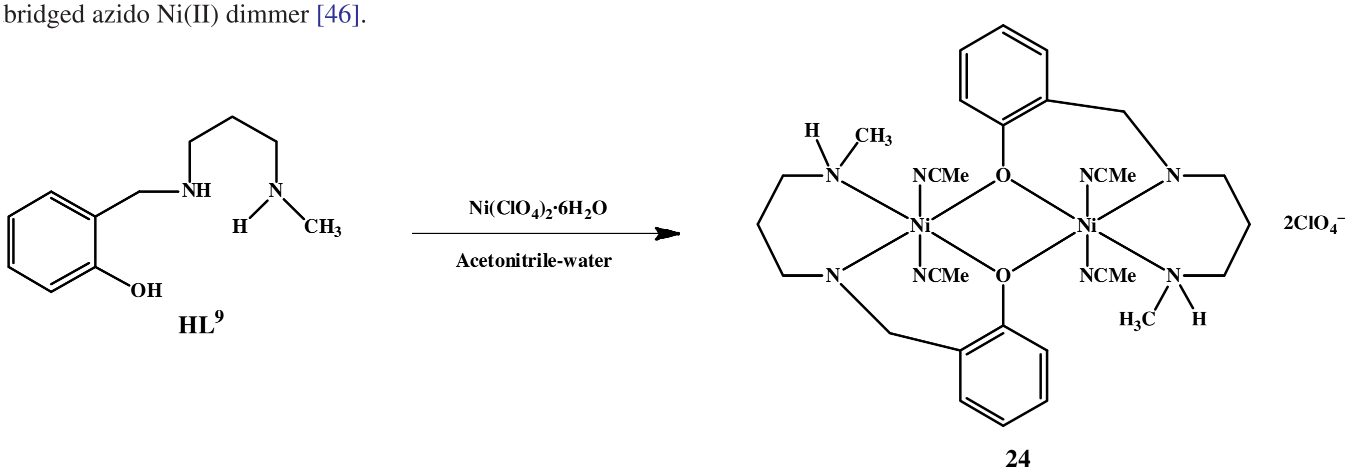
However a closer look at **Scheme-XII** reveals that these compounds can't be classified as pure NNO donor ligand complexes because although there is one NNO donor ligand attached to one Ni(II) center of the complex, the other Ni(II) center is linked to a different N/O donor moiety. There are quite a reasonable number of such examples [47-52] of hetero-hemisphere complexes where one among the ligands is NNO donor and another is N_2O_2 and the magneto structural data are also often fascinating. But as we are only focused on NNO donor ligands, the elaborate discussion is deferred as obviously their characteristic features are difficult to explain on the basis of the stereoelectronic implication of NNO ligand alone.

Synthesis of complex 24: For 30 min, the methanolic solution of Schiff base ligand HL^9 was reacted with an aqueous solution of $Ni(ClO_4)_2\cdot 6H_2O$ while being continuously stirred. The resultant green solution slowly evaporated, revealing a dark green micro-crystalline substance. Filtration was used to isolate the green solid, which was then washed with Et_2O and dissolved in CH_3CN. Slow evaporation of the acetonitrile solution produced dark green crystals of complex **24** with X-ray grade purity (**Scheme-XIII**) [28].

Structural revelation and magnetic property of complex 24: A distinct dimeric compound having a center of symmetry of formula $[Ni_2L^9(CH_3CN)_4](ClO_4)_2\cdot 2CH_3CN$ defines complex **24**. Two Ni(II) atoms connected by phenoxido oxygen atoms, with a Ni-Ni spacing of 3.207 Å and a Ni-O-Ni angle of 102.44º, make up the dinuclear core. Each nickel atom is octahedrally coordinated to two axial acetonitrile molecules, two phenoxido oxygen atoms and two N donors of the reduced Schiff base ligand (L^9). To keep the complex's charge balanced, there are two noncoordinated perchlorate anions present.

The temperature-dependent measurements of complex **24** of molar magnetic susceptibility show that at 300 K the $\chi_M T$ value is 2.11 $cm^3\ K\ mol^{-1}$, which is consistent with a non-interacting Ni^{2+} ion pair. The $\chi_M T$ exhibits a gradual decline upon cooling and, at 2 K, reaches a value of 0.01 $cm^3\ K\ mol^{-1}$. The aforementioned behaviour suggests a strong antiferromagnetic coupling in complex **24**.

Magnetostructural correlation of complex 24: The double phenoxido bridged Ni(II) dimmers exhibit antiferromagnetic properties and as the bridging angle increases, the coupling



Scheme-XIII: Synthetic procedure of the complex **24**

constant decreases. Plotting J values against the Ni-O-Ni bridging angle revealed that sign modification occurs at J values of ~97º [31]. The bridging angle Ni–O$_{(phenoxido)}$–Ni, 102.44(8)° in complex **24** suggests that strong antiferromagnetic interactions with J = -32.22 cm^{-1} should be observed.

Overall Magneto structural correlation for complexes 1-24: Numerous investigations on the magneto-structural correlations pertaining to dinuclear *bis*(phenoxido) bridged transition metal complexes have been published during the past 20 years. The majority of those investigations come to the conclusion that exchange coupling constant (J) clearly depend on phenoxido bridging angles. For instance, if the bridging angle is lower than the critical value ~97º, a *bis*(phenoxido) bridged Ni(II) dimer may exhibit ferromagnetic coupling; at larger angles, an antiferromagnetic coupling is anticipated [53]. In addition to the bridging angle, other significant parameters for the J values have been identified as the M-O$_{(phenoxido)}$ distance, the out-of-plane movement of the phenoxido ring system and the hinge deformation of M_2O_2 dinuclear framework [54-57]. According to published research, dinuclear diphenoxido bridged Ni(II) complexes often exhibit antiferromagnetic magnetic interactions, with the coupling constant growing increasingly negative with increasing bridging angle [58,59].

If the dimer consists of any additional single atom bridge (water, μ$_{1,1}$-azido, μ$_{1,1}$-thiocyanato, *etc.*) along with diphenoxido bridges then each of the three bridging groups should contribute to the resulting connection. When dealing with multiple bridged systems, the effects of the magnetic exchange through each bridge can be amplified or offset by varying interactions between the molecular orbitals concentrated on the bridging ligands with that of metal. These phenomena are referred to as orbital complementary and counter-complementary, respectively [60]. Stronger ferromagnetic coupling is known to be produced by bigger hinge angles and smaller phenoxido angles. It is important to remember that in the case of single atom bridging (phenoxido, water, hydroxide μ$_{1,1}$-isothiocyanato/isocyanato/azido, *etc.*), the ferromagnetic interaction reaches its peak at a bridging angle of around 90º. Below that point, it diminishes and eventually crosses over into the antiferromagnetic regions [31,61]. It has already been demonstrated that J and the bridging angle of single atom bridges have a parabolic connection. Ruiz *et al*. [62] demonstrated through theoretical research, that the ferromagnetic coupling of *bis*(μ$_{1,1}$-azido) complexes rises within the range of 87-104º with the Ni–N$_{(azido)}$–Ni angle. They also proposed that a low Ni–N$_{(azido)}$–Ni angle of about 84.2º can be found to exhibit weak antiferromagnetic behaviour. In comparison to diphenoxido bridged dinuclear complexes, the extra bridge folds the structure with a significant decrease in the phenoxido bridging angles. In the context of hetero-bridged systems, the counter-complementary consequences between the ligands, such as *syn-syn* carboxylates and N/O bridging nitrite, can result in both +ve and -ve inputs to the overall J value which define the observed ferromagnetic or antiferromagnetic behaviour.

Future perspectives: Due to their numerous and interdisciplinary applications, the structural and magnetic characteristics of dinuclear nickel(II) complexes of Schiff base ligands with polyatomic anions have shown to be a highly significant field of study. The presence of nickel(II) centres as the active metal site in any biochemically important enzymes is the primary reason for the ongoing interest in dinuclear Ni(II) species in the medical and pharmaceutical domains. They also have remarkable catalytic activity for a variety of chemical processes. Nonetheless, the possibility of employing dinuclear Ni(II) complexes with different bridging groups as molecular magnetic materials has sparked interest in the magnetic investigation of these complexes recently. The creation of the intended polynuclear complexes with Schiff bases and bridging ligands requires careful consideration. In particular, in combination with a few different bridging coligands like azide, cyanate, carboxylates, hydroxido, oxido, nitrite and nitrate, the tridentate NNO donor Schiff base ligands encourage the formation of multinuclear Ni(II) complexes with fascinating magnetic exchange interactions. Among the many paramagnetic transition metal centres, research on the structure and magnetic properties of octahedrally coordinated polynuclear Ni(II) complexes with tridentate Schiff base ligands and polyatomic anions yet to be explored in details. Thus, the formation of the new polynuclear Ni(II) complexes with various bridging groups is expected to contribute to a better understanding of the parameters controlling the coupling between the metal centres, which will help in the development and manufacturing of magnetic materials such as single-molecule magnets.

Conclusion

In this review, the synthetic protocol and magneto-structural features of 25 dinuclear nickel(II) complexes of tridentate NNO donor Schiff bases have been summarized. The Schiff bases are 1:1 condensation product of the N-substituted diammines with salicyldehyde or its analogues. Dinuclear Ni(II) complexes are synthesized using tridentate NNO donor Schiff base ligands in presence of various auxiliary bridging ligands, including carboxylates, pseudohalides, nitrate, nitrite, azide and dicyanamide. The complexes exhibit a clear sequence that highlights the dual functions, cooperating as well as competing role of the bridging phenoxido group and the monoanions used as bridging coligands. The previous explanation makes clear that the magnetic properties of different Ni(II) complexes are significantly influenced by structural parameters such as the Ni-O-Ni bridging angle and the Ni-Ni distance. Among the studied 25 dinuclear Ni(II) complexes, 14 complexes are antiferromagnetic whereas 11 complexes are ferromagnetic. Seven Ni(II) complexes are di-phenoxido bridged Ni(II) dimmers with Ni-O-Ni bridging angles >97º and are antiferromagnetically paired according to the magnetic investigation. Three nickel (II) compounds having a *syn-syn* carboxylato bridge in addition to the diphenoxido bridges show antiferromagnetic exchange interaction. A μ$_2$-1,3 carboxylate bridge can mediate additional exchange pathways with a counter-complementary effect to the phenoxido bridging and promote overall antiferromagnetic coupling. Two Ni(II) dimmer have 1kN:2kO nitrite bridging along with phenoxido briges and are antiferromagnetically coupled. Here, the hetero bridge (N/O bridging nitrito) enhance the antiferromagnetic contribution to the overall magnetic exchange interaction. There are seven complexes triply bridged by di-μ_2-phenoxido along with an water bridge. These seven complexes with reduced Ni-O-Ni bridging angles ranges from approximately 85 to 89º exhibit a moderate ferromagnetic coupling with positive *J* values. Another one triple bridged complex having end on thiocyanato bridge in addition to double phenoxido bridges posses lower bridging angle close to 90º and exhibits weak ferromagnetic coupling as expected from the bridging angle. Three more dinuclear Ni(II) complexes with pseudohalide bridging along with phenoxido bridge are also discussed. Among them, two behave ferromagnetically and one shows antiferromagnetic behaviour. Two more dinuclear Ni(II) complexes have to be special mention as they have no phenoxido bridges but with double $\mu_{1,1}$-azido and double $\mu_{1,5}$-dicyanamide bridges. Double $\mu_{1,1}$-azido bridged complex shows ferromagnetic coupling whereas the $\mu_{1,5}$-dicyanamide bridges mediates very weak antiferromagnetic interaction. Although the study of Schiff base and its transition metal complexes had been attracting the fascination of chemists for centuries still a wide area of synthesis, characterization and functionalization remains unexplored and hope this review will be an effective ancillary in this quest.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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